

Effects of Chromate Treatments on Environmental Stability of Lead/Tin Alloy Joints Bonded with an Ethylene–Acrylic Acid Copolymer. II. Failure Mechanism in Distilled Water

FUMIO YAMAMOTO, SHINZO YAMAKAWA, and MAKOTO WAGATSUMA, *Ibaraki Electrical Communication Laboratory, Nippon Telegraph and Telephone Public Corporation, Tokai, Ibaraki 319-11, Japan*

Synopsis

The environmental stability in distilled water and the failure mechanism of cathodically chromated tin, lead, and lead/tin alloy joints bonded with an ethylene–acrylic acid copolymer have been investigated by T-peel tests and ESCA and SEM analyses of the fractured surfaces. The peel strength of chromated lead/tin alloy joints and of both untreated and chromated tin joints is kept unchanged with water immersion, whereas that of untreated lead/tin alloy joints and of both untreated and chromated lead joints decreases rapidly with water immersion. ESCA and SEM observations show that lead/tin alloy surfaces consist of both lead and tin phases and that the tin phase interface deteriorates gradually with water immersion after premature deterioration of the lead phase interface. The stabilization effect of chromate treatments for lead/tin alloy joints is due to retardation of the underfilm corrosion of the tin phase.

INTRODUCTION

Cathodically chromated tin, lead and lead/tin alloy surfaces are covered with a corrosion-resistant chromate film consisting of highly hydrated chromium oxides.¹ The presence of the chromate film should improve the environmental durability of these metal joints bonded with ethylene–acrylic acid (EAA) copolymers. The previous article¹ has presented the details of the surface characterization of chromated tin, lead, and lead/tin alloys and the locus of failure in dry conditions of these metals bonded with an EAA copolymer. This article is concerned with the environmental stability of the adhesive joints in distilled water and the failure mechanism.

EXPERIMENTAL

The preparation of T-peel specimens and the T-peel testing are described in the previous article.¹ To evaluate the environmental stability in water, the peel specimens were immersed in distilled water at 50°C, and the T-peel strength was measured immediately at 25°C after water immersion. The locus of failure of wet joints was estimated from analysis of the fractured surfaces by x-ray photoelectron spectroscopy (ESCA) and scanning electron microscopy (SEM).

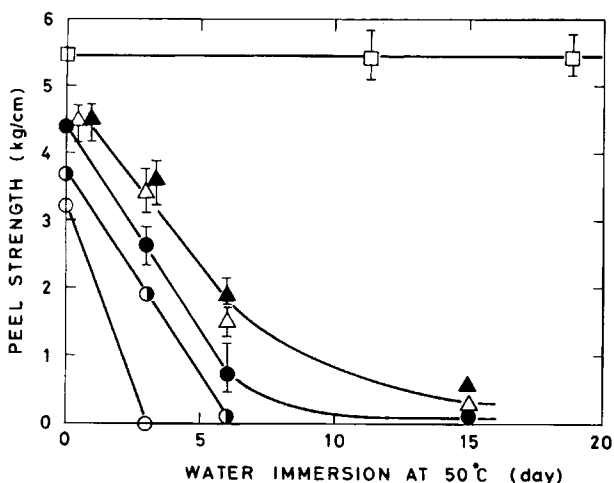


Fig. 1. Changes in peel strength of lead/tin alloy joints with exposure in distilled water at 50°C: (O) Pb; (●) 62% Pb; (●) 50% Pb; (Δ) 38% Pb; (▲) 20% Pb; (□) Sn.

RESULTS AND DISCUSSION

Water Immersion Test

Figure 1 shows the changes in peel strength with water immersion for lead/tin alloy joints, together with those for lead and tin joints. The peel strength of lead joints decreases rapidly with water immersion, whereas that of tin joints remains unchanged during water immersion (e.g., for more than 200 days at 50°C). The water resistance of lead/tin alloy joints is intermediate between those of lead and tin joints, and increases with increasing tin content of the alloy adherend. The water resistance, however, is poor even in an alloy joints of lead/tin 20/80. Since the peel strength of lead and lead/tin alloy joints did not decrease during storage in dry conditions, this decrease in peel strength is due to the deteriorative effects of water.

Figure 2 shows the water resistance of lead and lead/tin alloy joints cathodically chromated for 5 sec. Apparently, the chromate treatment enhances significantly

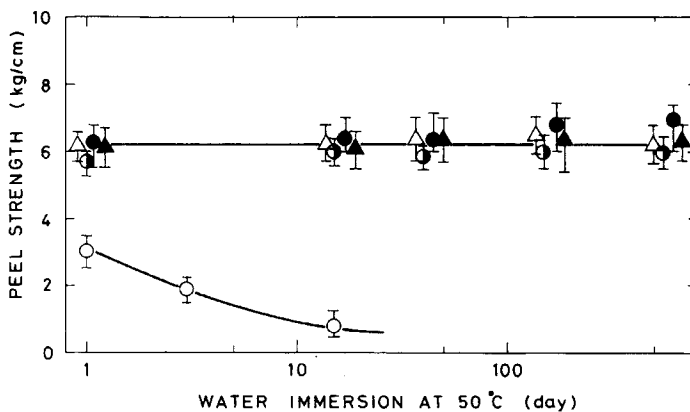


Fig. 2. Changes in peel strength of chromated lead and lead/tin alloy joints with exposure in distilled water at 50°C: (O) Pb; (●) 62% Pb; (●) 50% Pb; (Δ) 38% Pb; (▲) 20% Pb.

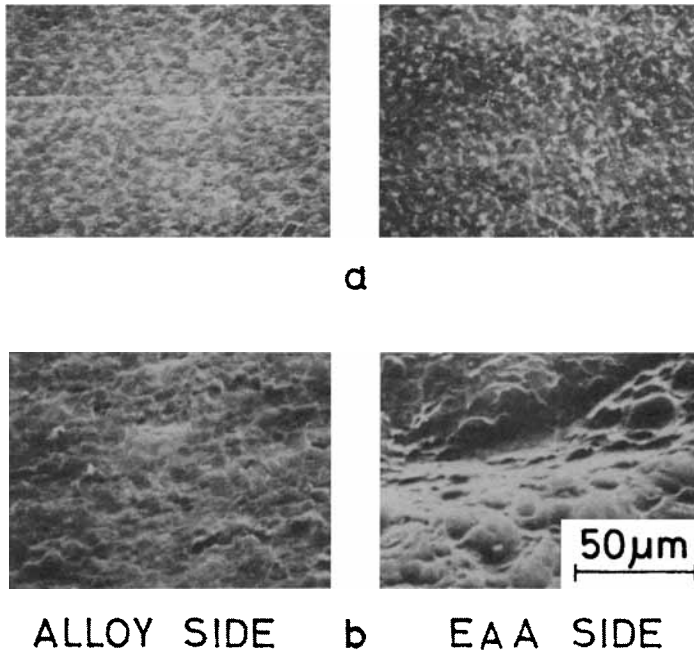


Fig. 3. SEM micrographs of peeled alloy (left) and adhesive (right) surfaces of untreated (a) and chromated (b) lead/tin 38/62 alloy joints fractured by T-peel test after immersion in distilled water at 50°C for 15 days.

the water resistance of lead/tin alloy joints, which retained the peel strength for 550 days at 50°C in the composition range of less than 80% Pb. On the other hand, chromated lead joints still have a poor water resistance, although they have higher resistance than untreated lead joints.

Locus of Failure

Figure 3 shows the SEM micrographs of fracture EAA and alloy surfaces of water-immersed lead/tin 38/62 alloy joints. Table I summarizes the ESCA composition ratios of the peeled surfaces corresponding to Figure 3. Untreated alloy joints yield low peel strength after water immersion (Fig. 1), and chromated

TABLE I
ESCA Composition Ratio from the Peeled Surfaces Corresponding to Figure 3

Surface	Composition ratio (at. %)						
	O	C	Sn		Pb		Cr
			Metal	Oxide	Metal	Oxide	Oxide
Original alloy	38.5	44.6	4.2	6.5	2.3	3.8	0
Original alloy, chromated	42.9	45.5	1.3	2.1	~0.4	0.9	7.0
Original EAA	9.6	90.4	0	0	0	0	0
Peeled alloy	23.4	58.5	3.7	8.2	2.8	3.4	0
Peeled EAA	14.6	84.5	0.1>	0.6	0.1>	0.1>	0
Peeled alloy, chromated	12.1	85.7	~0.2	0.7	~0.2	1.1	0.1>
Peeled EAA, chromated	12.6	85.9	0.1>	1.0	0.1>	~0.3	0.1>

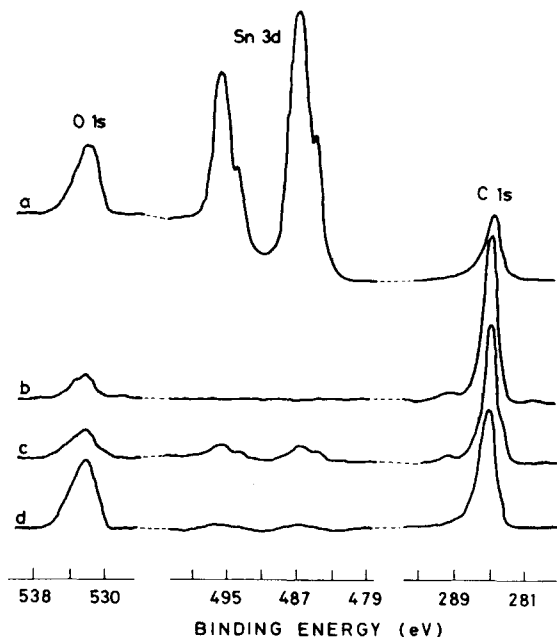


Fig. 4. ESCA spectra of peeled surfaces of tin joints: (a) original tin surface; (b) original EAA surface; (c) peeled tin surface; (d) peeled EAA surface.

joints retain the high peel strength even after water immersion (Fig. 2). The SEM micrographs (Fig. 3) of fractured EAA surfaces of the chromated alloy joints, peeled with high peel strength, show a significant plastic deformation of the EAA adhesive, whereas those of the untreated alloy joints peeled with low peel strength show a small plastic deformation of the adhesive. The fractured alloy surfaces of the chromated alloy joints show a significant decrease in Sn, Pb, and Cr ESCA peaks and an increase in C peak in comparison with the original alloy surface; i.e., both the peeled alloy and EAA surfaces show an overall EAA surface. These results indicate that bond failure occurs cohesively in the adhesive layer for chromated alloy joints accompanied by high peel strength and significant plastic deformation of the adhesive. On the other hand, for untreated alloy joints accompanied by low peel strength and small plastic deformation of the adhesive, ESCA observations indicate that failure occurs mainly at the

TABLE II
ESCA Composition Ratio of Peeled Surfaces of Water-Immersed Tin Joints

Surface	Composition ratio (at. %)			
	O	C	Sn	Cr
Original tin	31.0	55.7	13.3	0
Original tin, chromated	45.9	42.2	3.6	8.3
Original EAA	9.6	90.4	0	0
Peeled tin	6.6	92.5	0.9	0
Peeled EAA	7.0	92.8	~0.2	0
Peeled tin, chromated	9.1	90.0	0.7	~0.2
Peeled EAA, chromated	9.0	90.8	~0.2	0

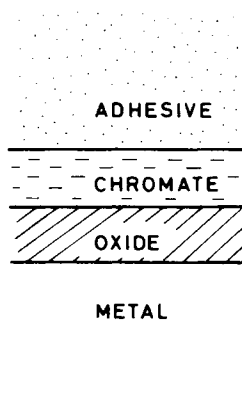


Fig. 5. Schematic representation of cross section of chromated lead/tin alloy joints.

alloy-EAA interface and partly in the alloy oxide layer. The fractured alloy and EAA surfaces show an ESCA composition ratio similar to those of the original alloy and EAA surfaces, respectively. However, the fractured EAA surface shows a slight appearance of tin peaks and a lower carbon peak than the original EAA surface; this indicates the transfer of a small amount of alloy oxide to the EAA side.

TABLE III
Changes in Locus of Failure with Water Immersion

Adherend	Locus of failure (peel strength)	
	Before water immersion	After water immersion
Lead	Oxide and oxide-metal interface (3-4 kg/cm)	Oxide-adhesive interface (interfacial separation)
Lead/tin alloy	Adhesive (4-5 kg/cm)	Oxide-adhesive interface and partly oxide (interfacial separation)
Tin	Adhesive (5-6 kg/cm)	Adhesive (5-6 kg/cm)
Lead, chromated	Oxide and oxide-metal interface (2.5-3.5 kg/cm)	Oxide and oxide-metal interface (ca. 1 kg/cm)
Lead/tin alloy, chromated	Adhesive (5-7 kg/cm)	Adhesive (5-7 kg/cm)
Tin, chromated	Adhesive (5-7 kg/cm)	Adhesive (5-7 kg/cm)

TABLE IV
Changes in Metal/Oxide Ratio of Lead/Tin Alloy Surfaces with Aging, Determined by ESCA

Surface	Tin metal/oxide composition Ratio		
	1 day in air	3 days in air	3 days in 60°C water
Lead	0 ^a	0 ^a	0 ^a
Lead/tin 62/38	0.6	0.3	0.2
Lead/tin 38/62	0.6	0.4	0.2
Lead/tin 38/62, chromated	0.3 ^b	0.3	0.3

^a Lead metal/oxide ratio.

^b The low initial ratio is due to the coverage of the surface with chromate film.

Both untreated and chromated tin joints retain the high peel strength during water immersion (Figs. 1 and 2), accompanied by significant plastic deformation of the adhesive. ESCA analysis of the peeled surfaces indicates the cohesive failure in the adhesive; both the fractured tin and EAA surfaces show an overall ESCA spectrum (Fig. 4) and an ESCA composition ratio (Table II) similar to the original EAA surface.

Water immersion of untreated lead joints caused rapid loss (Fig. 1) and interfacial separation whose failure occurred apparently at the EAA-lead interface. On the other hand, water immersion of chromated lead joints leads to rapid decrease in peel strength but not to interfacial separation (Fig. 2). ESCA analysis of the peeled surfaces showed the transfer of the chromate film to the EAA side; this indicates the failure between the chromate film and underlying lead; i.e., at the chromate film-lead oxide interface, in the lead oxide layer, or at the lead oxide-metal lead interface.

Failure Mechanism of Joints in Water

Figure 5 shows a schematic diagram of cross section of chromated lead/tin alloy joints. Table III summarizes the locus of failure of lead, tin, and lead/tin alloy joints, which were estimated by ESCA, SEM, and IMA analyses of the fractured surfaces. In general, the deterioration of metal-adhesive joints in water can be ascribed to (a) deterioration of the adhesive polymer, which was observed in lead/tin alloy-EAA joints in alkaline solutions,² (b) underfilm corrosion of the metal surface in contact with the adhesive,^{3,4} or (c) displacement of the adhesive by water^{5,6} (or rupture of the interfacial interactions and bonds by water). The underfilm corrosion process involves hydration of the surface oxide layer, the growth of a mechanically weak oxide layer,³ and the anodic dissolution of the underlying oxide layer.

Water immersion results in a rapid loss in peel strength and interfacial separation of lead sheet joints. This interfacial separation is probably due to the anodic dissolution of the surface lead oxide but not to the displacement of the adhesive by water.

Lead/tin alloy surfaces consist of lead and tin phases, as shown in Figure 6. The flat surface is tin phase and the rough surface is lead phase. The tin and lead phases were also verified by electron probe x-ray microanalysis⁷ (XMA). Accordingly, it can be assumed that the lead phase-EAA interface of alloy joints has a much lower water resistance than that of the tin phase-EAA interface. The lead phase interface of alloy joints may have a water resistance similar to that of the lead-EAA joint. The tin phase interface of alloy joints probably has a lower water resistance than that of the tin-EAA joint, since even an alloy of 80% Sn has a poor water resistance (Fig. 1). According to this two-phase model of alloy joints, water can access more easily the lead phase interface than the tin phase interface. After premature deterioration of the lead phase interface, the tin phase interface deteriorates gradually with water immersion time. The water resistance of lead/tin alloy joints is higher than that of lead joint and increases with increasing tin composition. This effect of the introduction of tin component can be explained in terms of the above two-phase model: the effect results from replacement of the lead surface by the water-resistant tin phase.

Chromate treatments enhance greatly the water resistance of lead/tin alloy

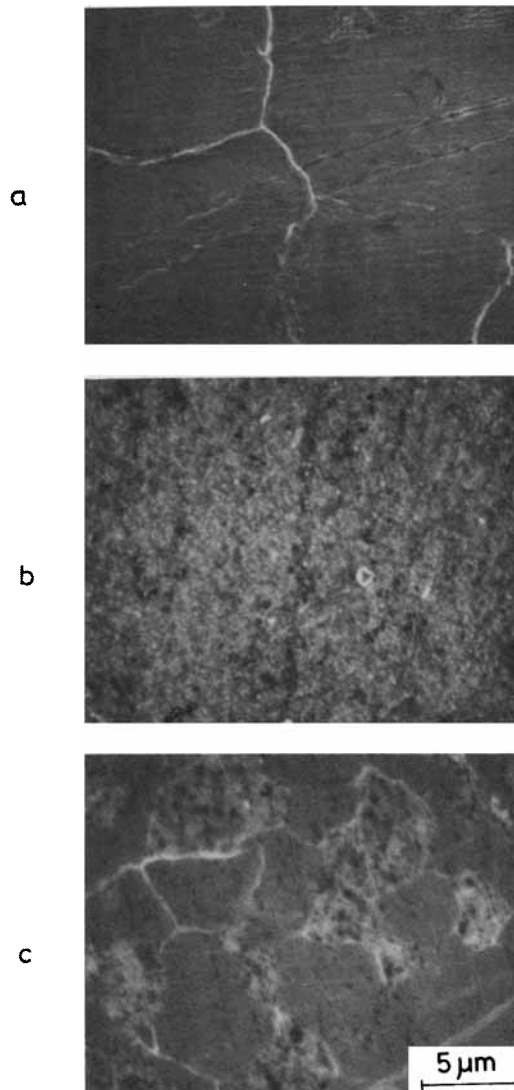


Fig. 6. SEM micrographs of (a) tin, (b) lead, and (c) lead/tin alloy surfaces.

joints, whereas they do not improve the water resistance of lead joint. This stabilization effect may be due to retardation of the underfilm corrosion of the tin phase, i.e., of the growth of the oxide layer and the anodic dissolution of the oxide layer. Table IV shows the changes in metal/oxide ratio with aging. In untreated lead/tin alloy surfaces, the metal/oxide ratio decreases with increasing aging time in air or water immersion. This result indicates the growth of the oxide layer. On the other hand, the metal/oxide ratio unchanges in chromated lead/tin alloy surfaces; i.e., the thickness of the oxide layer is kept at constant. These results indicate that the chromate film prevents the growth of the underlying alloy oxide layer. However, chromate treatment does not prevent completely the underfilm corrosion of the lead phase of alloy joints, since it does not prevent the rapid loss of peel strength of lead sheet joints.

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